

Code: 846-68535
Ref.: Johnson, N

JAPANESE PATENT OFFICE
PATENT JOURNAL
KOKAI PATENT APPLICATION NO. HEI 6[1994]-271509

Technical Disclosure Section

Int.Cl⁵

C 07 C 69/96
B 01 J 31/32
C 07 C 68/00
//C 07 B 61/00

Sequence Nos. for Office Use:

9279-4H
8017-4G
9279-4H

Application No.:

Hei 5[1993]-62149

Application Date:

March 22, 1993

Publication Date:

September 27, 1994

No. of Claims:

1 (Total of 5 pages; OL)

Examination Request:

Not requested

MANUFACTURE OF AROMATIC CARBONIC ACID ESTERS

Inventors:

Hiroshi Iwane
Mitsubishi Chemical Corp.
Tsuba Research Laboratory
8-3-1 Chuo-ku
Ami-machi,

2
Inashiki-gun, Ibaraki-ken

Takahiro Komeyama
Mitsubishi Chemical Corp.
Tsuba Research Laboratory
8-3-1 Chuo-ku
Ami-machi,
Inashiki-gun, Ibaraki-ken

Hidekazu Miyagi
Mitsubishi Chemical Corp.
Tsuba Research Laboratory
8-3-1 Chuo-ku, Ami-machi,
Inashiki-gun, Ibaraki-ken

Applicant:

000006057
Mitsubishi Chemical Corp.
2-5-2 Marunouchi
Chiyoda-ku, Tokyo

Agent:

Michiteru Soga, patent
attorney, and 6 others

Abstract

Objective

To offer a method for manufacturing aromatic carbonic acid esters by means of a reaction between an aromatic hydroxy compound, carbon monoxide and oxygen, where the aromatic carbonic acid ester can be manufactured at high concentrations and high yields in a short period of time using little catalyst.

Constitution

The reaction is carried out in the presence of (A) palladium or palladium compound, (B) one or more types of manganese compounds, (C) one or more types of cobalt compounds, (D) one or more types of substances selected from quaternary ammonium salts or quaternary phosphonium salts, and (E) one or more types of substances selected from quinones and aromatic diols that are reduction products thereof.

Claim

A method for manufacturing aromatic carbonic acid esters, wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, characterized in that said reaction is carried out in a reaction system in the presence of (A) one or more types of substances selected from palladium and palladium compounds, (B) one or more types of manganese compounds, (C) one or more types of cobalt compounds, (D) one or more types of substances selected from quaternary ammonium salts or quaternary phosphonium salts, and (E) one or more types of substances selected from quinones and aromatic diols that are reduction products thereof.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention concerns a method for the manufacture of aromatic carbonic acid esters using a special catalyst. Aromatic carbonic acid esters, particularly diphenyl carbonate, are useful as raw materials in the production of polycarbonate and other substances.

[0002]

Prior art

In the past, methods wherein an aromatic hydroxy compound and phosgene are allowed to react have been used as methods for manufacturing aromatic carbonic acid esters. However, these methods are undesirable due to the high toxicity of phosgene. Thus, a number of methods have been offered that do not use phosgene whereby aromatic carbonic acid esters are manufactured by a reaction between an aromatic hydroxy compound, carbon monoxide and oxygen. With regard to catalysts that are used in such methods, a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38144, wherein a palladium compound, a compound containing a metal from group IIIA, IVA, VA, VIA, IB, IIB, VIB or VIIB of the periodic table and a base are used; a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38145, wherein a palladium compound, manganese complex or cobalt complex, base and desiccant are used; a method is described in Japanese Kokai Patent Application No. Hei 1[1989]-165551, wherein a palladium compound, iodine compound and zeolites are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-104564, wherein a palladium compound, divalent or trivalent manganese compound, tetraalkylammonium halide and

quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-142754, wherein a palladium compound, cobalt compound, tetraalkylammonium halide and quinones are used; a method is described in U.S. Patent No. 5,142,086 and European Patent Application No. 507,546-A2, wherein a catalyst is used that comprises (a) palladium or palladium compound, (b) quaternary ammonium salt, (c) a metal auxiliary catalyst selected from cobalt, iron, cerium, manganese, molybdenum, samarium, vanadium, chromium and copper, and (d) an organic auxiliary catalyst selected from an aromatic ketone, an aliphatic ketone and an aromatic polycyclic hydrocarbon; and a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-25095, wherein palladium or palladium compound, cobalt compound, halide and basic compound are used. In addition, examples of methods that are used in order to prevent the hydrolysis of the aromatic carbonic acid esters due to water that is generated in the reaction include a method wherein a large quantity of desiccant is used (Japanese Kokai Patent Application No. Sho 54[1979]-135744), and a method wherein water is removed by distillation of the reaction (Japanese Kokai Patent Application No. Hei 4[1992]-261142).

[0003]

To generalize concerning catalyst systems that have been offered in the past, the systems can be conceived as being constituted by three components consisting of palladium catalyst + auxiliary catalyst + additives. In the reaction between the aromatic hydroxy compound, carbon monoxide and oxygen, aromatic carbonic acid ester is generated by the palladium catalyst under

acidic conditions, the auxiliary catalyst reoxidizes the palladium catalyst after the reaction, and the additives are used in order to accelerate said reaction. Manganese compounds or cobalt compounds are particularly useful as auxiliary catalysts, and compounds containing bromide ions are particularly useful as additives. In addition, the use of hydroquinone and other organic auxiliary catalysts or amines and other bases also appears to be effective.

[0004]

Problems to be solved by the invention

The inventors of the present invention et al. carried out additional tests on conventional technologies using phenol as a substrate, and discovered the following problems with conventional catalysts.

(i) When a manganese compound is used as the auxiliary catalyst, although the reaction progresses at a sufficiently high rate initially, the reaction stops halfway, and moreover, hydrolysis of the esters that are produced progresses due to the water that is co-produced;

(ii) the reaction is generally slow when a cobalt compound is used as a catalyst.

The present invention solves these problems with the aforementioned conventional catalyst systems, by perfecting an industrial method for the manufacture of aromatic carbonic acid esters. Specifically, the present invention makes it possible to manufacture aromatic carbonic acid esters at high space-time yields and reaction yields while maintaining high catalytic

activity. The objective of the present invention is to offer a method for manufacturing the target aromatic carbonic acid esters at high concentrations and high yields in a short period of time using little catalyst.

[0005]

Means to solve the problems

The inventors of the present invention et al. perfected the present invention upon discovering that the production efficiency of aromatic carbonic acid esters can be increased by using the special catalysts described below in specific amounts. The present invention is a method for manufacturing aromatic carbonic acid esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, characterized in that said reaction is carried out in the presence of (A) one or more types of substances selected from palladium and palladium compounds, (B) one or more types of manganese compounds, (C) one or more types of cobalt compounds, (D) one or more types of substances selected from quaternary ammonium salts or quaternary phosphonium salts, and (E) one or more types of substances selected from quinones and aromatic diols that are reduction products thereof.

[0006]

The inventors of the present invention et al., as a result of investigations concerning conventional technologies using phenol as a catalyst, discovered that the halfway stoppage of the reaction and hydrolysis of the ester product that occur when a

manganese compound is used as the auxiliary catalyst are caused by side reactions whereby the bromide ions in the additives are depleted as the phenol is converted to bromophenol via bromination. The present invention thus realizes an industrial method for manufacturing aromatic carbonic acid esters, wherein the by-production of bromophenols is controlled due to the synergistic action of the manganese compound and cobalt compound.

[0007]

Specific description of the invention

1. Reaction raw materials

(1) Aromatic hydroxy compound

The aromatic hydroxy compound that is used in the present invention is an aromatic mono- or polyhydroxy compound. Examples include phenol; cresol, xylenol, trimethylphenol, tetramethylphenol, ethylphenol, propylphenol methoxyphenol, ethoxyphenol, chlorophenol, dichlorophenol, bromophenol, dibromophenol and other substituted phenols and isomers thereof; naphthol, methylnaphthol, ethylnaphthol, chloronaphthol, bromonaphthol and other substituted naphthols and isomers thereof; 2,2-bis(4-hydroxyphenyl)propane and various other types of bisphenols; various types of biphenols; various types of heteroaromatic hydroxy compounds and isomers thereof; as well as compounds thereof produced by substitution with alkyl groups or halogen atoms. Of these compounds, phenol is particularly desirable.

[0008]

(2) Carbon monoxide

The carbon monoxide that is used in the present invention can be a gas that is produced by starting with a high-purity substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as nitrogen, argon or carbon dioxide.

[0009]

(3) Oxygen

The oxygen that is used in the present invention can be a gas that is produced by starting with a high-purity substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as air, nitrogen, argon or carbon dioxide.

[0010]

2. Catalyst

The catalyst that is used in the reaction of the present invention comprises the five components (A)-(E) below.

(A) Palladium or palladium compounds

The palladium and palladium compounds that are used in the present invention are palladium black; palladium carbon, palladium/alumina, palladium/silica or other carried palladium substances; palladium chloride, palladium bromide, palladium iodide, palladium sulfate, palladium nitrate or other inorganic palladium salts; and palladium acetate, palladium oxalate or other organic palladium acid salts. In addition, substances that can also be used include palladium(II) acetylacetonate, palladium complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins on palladium, examples of which include $\text{PdCl}_2(\text{PhCN})_2$, $\text{PdCl}_2(\text{PPh}_3)_2$, $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, $(\text{Pd}(\text{NH}_3)_4)\text{Cl}_2$, and $\text{Pd}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$, or mixtures of palladium with compounds generated by these complexes in the reaction system. Of these substances, organic acid palladium salts are preferred, with palladium acetate being particularly desirable. The amount of palladium component that is used in the reaction is in the range of 10^{-5} to 1 in terms of the moles ratio with respect to the aromatic hydroxy compound, with a range of 10^{-4} to 10^{-1} being preferred.

[0011]

(B) Manganese compound

The manganese compound that is used in the present invention is preferably a divalent or trivalent manganese compound, examples of which include manganese fluoride, manganese chloride, manganese bromide, manganese iodide, manganese sulfate, manganese carbonate, manganese nitrate and other inorganic salts; manganese formate, manganese acetate, manganese benzoate and other organic

acid salts; manganese(II) or (III) acetylacetonate, complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins on manganese; and mixtures of manganese salts and compounds formed in the reaction system by these complexes. There are no particular restrictions on the amount of manganese component that is used in the reaction, but a molar ratio in the range of 10^{-3} to 10^2 with respect to the palladium component (A) is preferred, with a range of 10^{-2} to 10 being particularly desirable.

[0012]

(C) Cobalt compound

Examples of cobalt compounds that are used in the present invention are preferably divalent or trivalent cobalt compounds, such as cobalt fluoride, cobalt chloride, cobalt bromide, cobalt iodide, cobalt sulfate, cobalt carbonate, cobalt nitrate, cobalt hydroxide and other inorganic salts, cobalt formate, cobalt acetate and other organic acid salts; cobalt(II) or (III) acetylacetonate or complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins on cobalt; and mixtures of cobalt and compounds that are generated in the reaction system by these complexes. The amount of cobalt compound that is used in the reaction has no particular restrictions, but a molar ratio in the range of 10^{-4} - 10^2 with respect to the palladium component (A) is preferred, with a range of 10^{-3} - 10 being particularly desirable.

[0013]

(D) Quaternary ammonium salt or quaternary phosphonium salt
(Sometimes referred to hereinafter as "quaternary onium salts")

The quaternary ammonium salt that is used in the present invention is a compound that is expressed by the formula $R^1R^2R^3R^4N^+X^-$ or $R^1R^2R^3R^4P^+X^-$. In the formula, R^1-R^4 can be the same or different, and denote alkyl groups with carbon numbers of 1-8 or aryl groups with carbon numbers of 6-12. Examples include methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, hexyl groups, octyl groups, cyclohexyl groups, phenyl groups, tolyl groups, xylyl groups and naphthyl groups. X^- denotes an anion, examples of which include a hydroxide ion, chloride ion, bromide ion, iodide ion or other halide anion; or phenoxide anion, acetate anion or other organic anion. Halide ions are preferred, with bromide ions being preferred among these. Specific examples include tetra-n-ethylammonium bromide, tetra-n-butylammonium bromide and tetraphenylphosphonium bromide. The amount of quaternary ammonium salt that is used in the reaction is preferably in the range of a molar ratio of 10^{-2} to 10^3 with respect to the palladium component (A), with a range of 10^{-1} to 10^2 being the most preferred.

[0014]

(E) Quinones and aromatic diols that are reduction products thereof

Examples of quinones and aromatic diols that are reduction products thereof include 1,4-quinone, 1,2-quinone, catechol,

3
naphthoquinone, anthraquinone and hydroquinone. Of these substances, 1,4-quinone and hydroquinone are particularly desirable. There are no particular restrictions on the used amount of these compounds, but because there is a tendency for the reaction to be inhibited when these compounds are used in too great an excess, a range of 10^{-1} to 10^3 in terms of molar ratio with respect to the palladium or palladium compound is used, with a range of 1 to 10^2 being preferred.

[0015]

3. Reaction conditions

The reaction is performed by introducing the aforementioned aromatic hydroxy compound and components (A), (B), (C), (D) and (E) into the reactor, pressurizing the system with carbon monoxide and oxygen, and carrying out the reaction while heating. The reaction pressure is in the range of 0.1-500 atm, with 1-250 atm being preferred. It is preferable for the compositional ratio of carbon monoxide and oxygen to be far from the combustion range. The reaction temperature is in the range of 20-300°C, with 60-250°C being preferred, and 80-150°C being additionally desirable. The reaction time is a few minutes to a few hours. Examples of solvents that can be used in the reaction include hexane, heptane, cyclohexane, benzene, toluene, xylene, methylene chloride, chloroform, chlorobenzene, diethyl ether, diphenyl ether, tetrahydrofuran, dioxane, ethyl acetate, methyl formate, acetonitrile and other inert solvents. There are cases where the raw material aromatic hydroxy compound serves as the reaction

solvent, and it is not particularly necessary to use another solvent in such cases.

[0016]

Application examples

The present invention is described in detail below by providing application examples and comparative examples.

Application Example 1

3.5 g (37 mmol) phenol, 25.6 mg (12 μ g-atom) of 5% palladium/carbon, 3.0 mg (12 μ mol) manganese(II) acetate tetrahydrate, 0.74 mg (3.0 μ mol) cobalt(II) acetate tetrahydrate, 77 mg (0.24 mmol) tetra-n-butylammonium bromide, and 13 mg (0.12 mmol) hydroquinone were introduced into a Hastelloy autoclave with a volume of 30 mL. The interior of the system was replaced with carbon monoxide, which was introduced at 60 atm, while dry air was introduced at 30 atm. The reaction was carried out for 3 h at 100°C while stirring with a stir bar. After completion of the reaction, the reaction solution was analyzed by gas chromatography. The results indicated that diphenyl carbonate was obtained at a yield of 19% (3.5 mmol). The by-production of o- and p-bromophenol was not seen.

[0017]

Application Example 2

The same reaction as in Application Example 1 was carried out, with the exception that the reaction time was increased to 5h. Carbonic acid ester was obtained at a yield of 24% (4.4 mmol). In addition, o- and p-bromophenol were obtained at a total amount of 12% (29 μ mol) with respect to the bromide.

[0018]

Comparative Example 1

A reaction was carried out in the same manner as in Application Examples 1 and 2, with the exception that cobalt(II) acetate tetrahydrate was not used. After reacting for 3 h, the carbonic acid ester yield was 7.4% (1.4 mmol), and o- and p-bromophenol were obtained as by-products at a total amount of 91% (0.22 mmol) with respect to the bromide. After reacting for 5 h, the carbonic acid ester amount had decreased to a yield of 4.7% (0.87 mmol), and the total amount of o- and p-bromophenol was 93% (0.22 mmol) with respect to the bromide.

[0019]

Comparative Example 2

A reaction was carried out in the same manner as in Application Examples 1 and 2, with the exception that manganese(II) acetate tetrahydrate was not used. After reacting for 3 h, the carbonic acid ester yield was 12% (2.1 mmol), and the by-production of o- and p-bromophenol was not seen. After reacting for 5 h, carbonic acid ester had increased slightly to a yield of 12% (2.2 mmol), and o- and p-bromophenol were

by-produced at a total of 11% (26 μmol) with respect to the bromide.

[0020]

Application Example 3

The same reaction as in Application Example 1 was carried out, with the exception that 2.7 mg (12 μmol) palladium(II) acetate were used instead of the 5% palladium/carbon. The results gave a carbonic acid ester yield of 15% (2.8 mmol), and no by-production of o- and p-bromophenol was seen.

[0021]

Application Example 4

A reaction was carried out in the same manner as in Application Example 1, with the exception that 4.2 mg (12 μmol) manganese(III) acetoacetate were used instead of manganese(II) acetate tetrahydrate. The results indicated a carbonic acid ester yield of 20% (3.7 mmol), and no by-production of o- and p-bromophenol was seen.

[0022]

Application Example 5

A reaction was carried out in the same manner as in Application Example 1, with the exception that 1.1 mg (3.0 μmol)